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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: SINGLE STEP PROCESS FOR THE PREPARATION OF LOWER α -ALKENE POLYMERIZATION HETEROGENEOUS SOLID CATALYST

(57) Abstract: Single step process for the preparation of lower α -alkene polymerisation heterogeneous solid catalyst, wherein the procatalyst is obtained by reacting organomagnesium precursor and titanium tetrahalide or titanium haloalkoxo species of the formula $Ti(OR)_m X_n$, with a hydrocarbon or haloalkohydrocarbon solvent and internal electron donor and optionally an acid halide under microwave irradiation of 300 to 1200 W. The mole ratio of the organomagnesium precursor to the titanium tetrachloride or titanium haloalko species is 1: 6 to 1:20 and the mole ratios of the electron donor and acid halide to titanium is 0.3 to 1.5 and 0.02 to 0.2, respectively.



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TITLE OF INVENTION

Single step process for the preparation of lower α -alkene polymerization heterogeneous solid catalyst.

This invention also relates to lower α -alkene polymerisation heterogeneous solid catalyst obtained by the single step process and process for the polymerization of lower α -alkene using the heterogeneous solid catalyst.

BACKGROUND ART

Polymers of lower α -alkene or olefins such as ethylene, propylene or 1-butene find applications in the manufacture of a variety of articles including plastic bags or sheets or automobile parts. Of particular interest in polymer production are polyethylene and polypropylene with a high degree of isotacticity i.e. the extent of orientation of the branched groups in the polymer in the same direction, which shows high crystallinity. The polymerisation involves reacting the lower α -alkene such as ethylene or propylene with catalyst under polymerisation conditions. The early polymerisation catalysts were of relatively low activity and the polymers formed contained significant amounts of the

catalyst residues, which had to be removed by deashing. The more recent alkene polymerisation catalysts are of two types viz. single site catalysts and heterogeneous solid catalysts. The single site catalysts comprise metallocene and non-metallocene complexes of transition metals and a cocatalyst such as methyl aluminoxane and produces polymer of low polydispersity.

Heterogeneous solid catalysts are the most commonly used catalysts, especially in the bulk production of polyethylene or polypropylene due to their high activity and ease of operation. These catalysts are sometimes referred to as heterogeneous Ziegler-Natta catalysts. A heterogeneous solid catalyst comprises a procatalyst and a cocatalyst and for polypropylene with high isotacticity an external selectivity control agent or external electron donor also. The cocatalyst may be an organoaluminium compound such as alkyl aluminium. The physicochemical properties of the procatalyst play a pivotal role in the overall performance of the catalysts. The procatalysts comprise organomagnesium or magnesium chloride derived precursor comprising magnesium chloride supported titanium chloride and an internal electron donor. The procatalysts are synthesised by halogenation of an organomagnesium

compound such as magnesium ethoxide with a halogenating agent such as titanium tetrahalide in a hydrocarbon or halohydrocarbon solvent such as toluene or chlorobenzene optionally with an acid halide to form magnesium chloride. The magnesium chloride so obtained is reacted with
5 titanium haloalkoxide or excess titanium tetrahalide, usually titanium tetrachloride in the presence of a hydrocarbon or a halohydrocarbon solvent. To this an internal electron donor is added simultaneously or sequentially to result in a procatalyst (US Patents Nos 4400302, 4,414,132, 4,497,905, 4,535,068, 4,657,995, 4,710,482, 4,728,705, 4,771,024, 4,804,648, 4,870,039, 4,914,069, 4,870,040, 5,066,737, 5,077,357, 5,106,806, 5,082,907,
10 5,122,494, 5,124,298, 5,141,910, 5,151,399 and 5,229,342). In most of the above processes employing organomagnesium compounds or silica coated with organomagnesium compounds, the procatalyst preparation involves treatment of the magnesium precursor with titanium tetrahalide more than
15 once, so that catalysts of optimum titanium loading and activity are obtained. US Patents Nos 4400302 and 4,414,132 teach that at least two treatments with titanium tetrahalide are required for catalysts with high activity. In US Patents Nos 4,497,905, 4,535,068 and 4,657,995, where a halogenating agent is used to enhance activity, several treatments with

titanium tetrachloride are described. The total amounts of titanium tetrahalide required for multiple treatments are also considerable.

Procatalyst also may be prepared by milling together
5 anhydrous magnesium chloride, a titanium tetrahalide such as titanium tetrachloride and for polypropylene catalyst an internal electron donor (US Patents Nos 4329253, 4393182 and 4419501). Preparation of procatalysts by this physical method requires very long milling time. Furthermore when used in polymerisation reactions, procatalysts obtained
10 by milling in general show activities and selectivities inferior to those obtained by chemical method.

Several processes and products employing microwave energy are reported in patent literatures. PCT Publication No
15 WO2001028771 describes microwave curable compositions comprising at least one heat curable resin component, microwave absorbable particles in an amount of about 10% of the composition, and at least one curing agent for the heat curable resin component. European Patent no 992480 describes the preparation of methacrylate esters and polyester
20 methacrylates in the presence of a catalyst and inhibitor under microwave

heating. US Patent Nos 6017845 and 6171479 describe a process that involves a catalyst comprising a support, a microwave absorption material and catalytically active phase. On heating the catalyst with a source of microwave energy, the microwave absorption material absorbs the energy and increases the temperature of the catalyst to the desired level. The heated catalyst is contacted with a hydrocarbon feedstock for upgrading. PCT Publication No WO 9743230 describes a method for palladium catalyzed organic reactions heated with microwave energy in solution. US Patent No 5194514 describes the use of microwave in the presence of paramagnetic catalysts to increase molecular weight of the polymer. US Patent No 5719095 describes supported catalyst system comprising support, at least one metallocene catalyst fixed to the support, and at least one cocatalyst, wherein the catalyst is fixed to the support by bringing the catalyst into contact with a supported cocatalyst in a suspension and irradiating with microwaves.

OBJECTS OF INVENTION

An object of the invention is to provide single step process for the preparation of lower α -alkene polymerisation heterogeneous

solid catalyst which simplifies the preparation procedure and shortens the preparation time.

Another object of the invention is to provide single step
5 process for the preparation of lower α -alkene polymerisation heterogeneous solid catalyst which reduces the amount of titanium tetrahalide required and is economical.

Another object of the invention is to provide single step
10 process for the preparation of lower α -alkene polymerisation heterogeneous solid catalyst, which when used in polymerisation of ethylene and propylene shows high activity and selectivity and for propylene results in polymers with high isotacticity index.

15 DETAILED DESCRIPTION OF INVENTION

According to the invention there is provided a single step
process for the preparation of lower α -alkene polymerisation heterogeneous solid catalyst comprising an organomagnesium precursor
20 derived procatalyst comprising magnesium chloride supported titanium

chloride and an internal electron donor and an organoaluminium compound based cocatalyst, wherein the mole ratio of aluminium in the cocatalyst to titanium in the procatalyst is 10 - 3000 : 1 and the procatalyst is obtained by single step reaction of organomagnesium precursor and titanium tetrahalide or titanium haloalkoxo species of the formula $Ti(OR)_m X_n$, wherein R is methyl, ethyl, normal or isopropyl, normal or isobutyl, preferably n-butyl, X is chlorine or bromine, preferably chlorine and $m + n = 4$ with the condition that when $m = 1 - 4$, $n = 3 - 0$ respectively with a hydrocarbon or haloalkane solvent and internal electron donor and optionally an acid halide under microwave irradiation of 300 to 1200 W followed by isolating the procatalyst, the mole ratio of the organomagnesium precursor to the titanium tetrachloride or titanium haloalko species being 1: 6 to 1:20 and the mole ratios of the electron donor and acid halide to titanium being 0.3 to 1.5 and 0.02 to 0.2, respectively.

According to the invention there is also provided a single step process for the preparation of polypropylene polymerisation heterogeneous solid catalyst comprising an organomagnesium precursor derived procatalyst comprising magnesium chloride supported titanium chloride

and an internal electron donor and an organoaluminium compound based cocatalyst and a selectivity control agent, wherein the mole ratio of aluminium in the cocatalyst to titanium in the procatalyst is 10 - 3000 : 1 and the mole ratio of selectivity control agent to titanium is 10 - 100 : 1 and the procatalyst is obtained by single step reaction of organomagnesium precursor and titanium tetrahalide or titanium haloalkoxo species of the formula $Ti(OR)_m X_n$, wherein R is methyl, ethyl, normal or isopropyl, normal or isobutyl, preferably n-butyl, X is chlorine or bromine, preferably chlorine, $m = 0$ and $n = 4$ with a hydrocarbon or haloalkohydrocarbon solvent and an internal electron donor and optionally an acid halide under microwave irradiation of 300 to 1200 W followed by isolating the procatalyst, the mole ratio of the organomagnesium precursor to the titanium tetrachloride or titanium haloalko species being 1: 6 to 1:20 and the mole ratios of the electron donor and acid halide to titanium being 0.3 to 1.5 and 0.02 to 0.2 respectively.

Preferably the mole ratio of the aluminium in the cocatalyst to the titanium in the procatalyst of the catalyst is 200:1.

The heterogeneous solid procatalyst may have a surface area of 40-300 m²/g, preferably 50 - 200 m²/g.

The titanium tetra halide may be titanium tetra chloride or
5 bromide, preferably titanium tetra chloride.

The organomagnesium precursor such as magnesium ethoxide and anhydrous magnesium chloride used for preparation of the procatalyst are commercially available or prepared in known manner.

10 Other magnesium alkoxides such as methoxide, normal and isopropoxide, normal and isobutoxide and 2-ethyl butoxide may also be used but the preferred organomagnesium precursor is magnesium ethoxide.

15 The hydrocarbon or halohydrocarbon solvent used in the reaction must be capable of absorbing microwave energy and may be hexane, methyl cyclohexane, toluene, xylene, chlorobenzene, dichlorobenzene or o-chlorotoluene, the preferred solvent being chlorobenzene.

Preferably, a microwave energy of 300 W is applied.

The isolation of the procatalyst involves filtration, washing with a hydrocarbon solvent such as toluene and drying of the solid.

5

The organoaluminium cocatalyst may be trialkyl or mixed halo alkyl or alkoxo aluminium compounds usually employed with titanium procatalysts. These may be commercially available or prepared in known manner. Preferably triethyl aluminium is used.

10

Preferably, the mole ratio of the organomagnesium precursor to the titanium tetrachloride or titanium haloalko species is 1:13.

15

The selectivity control agent is an ester such as p-substituted benzoate or phthalate ester, preferably p-ethoxy ethyl benzoate or an ether such as alkyl alkoxy or aryl alkoxy silane. Preferably dicyclohexyl dimethoxy silane or diphenyl dimethoxy silane usually employed with titanium procatalysts are used. The selectivity control agents may be commercially available or prepared in known manner. Preferably

the mole ratio of the selectivity control agent to the titanium in the procatalyst is 10 - 75 : 1.

The internal electron donor may be esters of benzoic acid or diesters of phthalic acid preferably ethyl benzoate, dibutyl or diisobutyl phthalate.

The acid halide may be halide of an aliphatic or aromatic acid preferably benzoyl chloride.

Preferably the molar ratios of the electron donor and acid halide if any to titanium are 0.7 and 0.07, respectively.

The constituents of the polymerisation catalyst viz. procatalyst and cocatalyst and optionally selectivity control agent may be mixed in a vessel outside the polymerisation reactor before being transferred to the polymerisation reactor. Alternatively, the constituents may be individually transferred into the polymerisation reactor to generate the active catalyst in situ.

The lower α -alkenes used for polymerisation may be ethylene, propylene, 1-butene or 1-hexene to produce homopolymers or copolymers. Preferably ethylene or propylene is used. The polymerisation may be conducted with one or more lower α -alkene to produce
5 homopolymers or copolymers, in the gas phase employing one or more fluidized beds of catalysts in known manner. Alternatively, the polymerisation may be conducted in the slurry phase in the absence or presence of an inert hydrocarbon diluent such as hexane in known manner.

10 According to the invention the polymerisation catalyst is prepared in one step reaction. This simplifies the procatalyst manufacturing procedure and reduces the batch time. The amount of titanium tetrahalide used for making the procatalyst is also reduced thereby rendering the process economical. The procatalyst prepared by
15 the process of the invention shows high activity and selectivity, particularly in producing polymers with high isotacticity index.

The following experimental examples are illustrative of the invention but not limitative of the scope thereof.

Example 1

Magnesium ethoxide (10 gm) and TiCl_4 (131 ml) diluted with chlorobenzene (131 ml) were placed inside a multi necked quartz flask equipped with nitrogen inlet, electronic temperature sensor probe and reflux condenser. The mixture was magnetically stirred and the temperature of the mixture was maintained at 110°C for one hour under microwave radiation 300W. The yellowish solid formed was filtered, washed twice with hexane and dried under a stream of nitrogen.

Example 2

Magnesium ethoxide (10 gm) and TiCl_4 (90 ml) and $\text{Ti}(\text{O}i\text{Bu})_4$ (40 ml) diluted with chlorobenzene (131 ml) were placed inside a multi necked quartz flask equipped with nitrogen inlet, electronic temperature sensor probe and reflux condenser. The mixture was magnetically stirred and the temperature of the mixture was maintained at 110°C for one hour under microwave radiation 300W. The yellowish solid formed was filtered, washed twice with hexane and dried under a stream of nitrogen.

Example 3

Magnesium ethoxide (10 gm) and TiCl_4 (131 ml) diluted with chlorobenzene (131 ml) in the presence of ethyl benzoate (8.4 ml) and benzoyl chloride (0.7 ml) were placed inside a multi necked quartz flask equipped with nitrogen inlet, electronic temperature sensor probe and reflux condenser. The mixture was magnetically stirred and the temperature of the mixture was maintained at 110°C for one hour under microwave radiation 300W. The yellowish solid formed was filtered, washed twice with hexane and dried under a stream of nitrogen.

Example 4

Magnesium ethoxide (10 gm) and TiCl_4 (131 ml) diluted with chlorobenzene (131 ml) in the presence of diisobutyl phthalate (3.9 ml) and benzoyl chloride (0.7 ml) were placed inside a multi necked quartz flask equipped with nitrogen inlet, electronic temperature sensor probe and reflux condenser. The mixture was magnetically stirred and the temperature of the mixture was maintained at 110°C for one hour under microwave radiation (300W). The yellowish solid formed was filtered, washed twice with hexane and dried under a stream of nitrogen.

Example 5

Anhydrous magnesium chloride (10 gm) and TiCl_4 (131 ml) diluted with chlorobenzene (131 ml) in the presence of ethyl benzoate (8.4 ml) were placed inside a multi necked quartz flask equipped with nitrogen inlet, electronic temperature sensor probe and reflux condenser. The mixture was magnetically stirred and the temperature of the mixture was maintained at 110°C for one and a half hour under microwave radiation 300W. The yellowish solid formed was filtered, washed twice with hexane and dried under a stream of nitrogen.

Example 6

Anhydrous magnesium chloride (10 gm) and $\text{Ti}(\text{O}i\text{Bu})_4$ (170 ml) diluted with chlorobenzene (170 ml) were placed inside a multi necked quartz flask equipped with nitrogen inlet, electronic temperature sensor probe and reflux condenser. The mixture was magnetically stirred and the temperature of the mixture was maintained at 110°C for one and a half hour under microwave radiation 600W. The pale yellow solid formed was filtered, washed twice with hexane and dried under a stream of nitrogen.

Example 7

In the presence of cocatalysts and for propylene in the presence of external electron donors, the procatalysts obtained in Example 1 to 6 were used for polymerization reactions of lower α -alkenes. The polymerization data are given in the following Table. The polymerization reactions were carried out under two sets of conditions: A and B. Polymerizations under conditions A were carried out in the slurry phase with hexane as the diluent under a constant pressure of 5 Kg for 1 hr at 70° C. The procatalyst (0.1 gm) was mixed with triethyl aluminium co-catalyst (1.425 gm) and for propylene either p-ethoxy ethyl benzoate (0.61 gm) or dicyclohexyl dimethoxy silane (0.15 gm) as the selectivity control agent. Polymerization under conditions B were carried out in the slurry phase with hexane as the diluent under atmospheric pressure at 30° C. The procatalyst (0.1 gm) was mixed with triethyl aluminium co-catalyst (1.425 gm) and for propylene either p-ethoxy ethyl benzoate (0.61 gm) or dicyclohexyl dimethoxy silane (0.15 gm) was used as the selectivity control agent.

TABLE

| Procatalyst | α -Alkene | Condition | Polymer yield (gm per 0.1 gm of procatalyst)/ Selectivity |
|-------------|------------------|-----------|--|
| Example 1 | Ethylene | A | 450 |
| Example 2 | Ethylene | A | 400 |
| Example 3 | Propylene | B | 300 / 96 % |
| Example 4 | Propylene | B | 280 / 97.5% |
| Example 5 | Propylene | B | 150 / 96% |
| Example 6 | Ethylene | A | 350 |

The table shows that the catalyst prepared by the single step process has excellent activity and selectivity for the polymerization of ethylene and propylene.

CLAIMS

1. Single step process for the preparation of lower α -alkene polymerisation heterogeneous solid catalyst comprising an organomagnesium precursor derived procatalyst comprising magnesium chloride supported titanium chloride and an internal electron donor and an organoaluminium compound based cocatalyst, wherein the mole ratio of aluminium in the cocatalyst to titanium in the procatalyst is 10 - 3000 : 1 and the procatalyst is obtained by single step reaction of organomagnesium precursor and titanium tetrahalide or titanium haloalkoxo species of the formula $Ti(OR)_m X_n$, wherein R is methyl, ethyl, normal or isopropyl, normal or isobutyl, preferably n-butyl, X is chlorine or bromine, preferably chlorine and $m + n = 4$ with the condition that when $m = 1 - 4$, $n = 3 - 0$ respectively with a hydrocarbon or halohydrocarbon solvent and internal electron donor and optionally an acid halide under microwave irradiation of 300 to 1200 W followed by isolating the procatalyst, the mole ratio of the organomagnesium precursor to the titanium tetrachloride or titanium haloalko species being 1: 6 to 1:20 and the mole ratios of the electron donor and acid halide to titanium being 0.3 to 1.5 and 0.02 to 0.2, respectively.

2. Single step process as claimed in claim 1, wherein the organomagnesium precursor is magnesium ethoxide.

5 3. Single step process as claimed in claim 1, wherein the mole ratio of the organomagnesium precursor to the titanium tetrachloride or titanium haloalkoxo species is 1:13.

10 4. Single step process as claimed in claim 1, wherein the titanium tetrahalide is titanium tetrachloride.

5. Single step process as claimed in claim 1, wherein the mole ratio of aluminium in the cocatalyst to titanium in the procatalyst is 200 : 1.

15 6. Single step process as claimed in claim 1, wherein the solvent is chlorobenzene.

7. Single step process as claimed in claim 1, wherein the microwave radiation of 300 W is applied.

8. Single step process as claimed in claim 1, wherein the organoaluminium compound is triethyl aluminium.

9. Single step process as claimed in claim 1, wherein the molar ratios of the electron donor and acid halide, if any, to titanium are 0.7 and 0.07 respectively.

10. Single step process as claimed in claim 1, wherein the electron donor is ethyl benzoate, dibutyl or diisobutyl phthalate.

11. Single step process as claimed in claim 1, wherein the acid halide is benzoyl chloride.

12. Lower α -alkene polymerisation heterogeneous solid catalyst obtained by the single step process as claimed in any one of claims 1 to 11.

13. Single step process for the preparation of polypropylene polymerisation heterogeneous solid catalyst comprising an organomagnesium precursor derived procatalyst comprising magnesium

chloride supported titanium chloride and an internal electron donor and an organoaluminium compound based cocatalyst and a selectivity control agent, wherein the mole ratio of aluminium in the cocatalyst to titanium in the procatalyst is 10 - 3000 : 1 and the mole ratio of selectivity control agent to titanium is 10 - 100 : 1 and the procatalyst is obtained by single step reaction of organomagnesium precursor and titanium tetrahalide or titanium haloalkoxo species of the formula $Ti(OR)_m X_n$, wherein R is methyl, ethyl, normal or isopropyl, normal or isobutyl, preferably n-butyl, X is chlorine or bromine, preferably chlorine, $m = 0$ and $n = 4$ with a hydrocarbon or haloalkohydrocarbon solvent and an internal electron donor and optionally an acid halide under microwave irradiation of 300 to 1200 W followed by isolating the procatalyst, the mole ratio of the organomagnesium precursor to the titanium tetrachloride or titanium haloalko species being 1: 6 to 1:20 and the mole ratios of the electron donor and acid halide to titanium being 0.3 to 1.5 and 0.02 to 0.2 respectively.

14. Single step process as claimed in claim 13, wherein the organomagnesium precursor is magnesium ethoxide.

15. Single step process as claimed in claim 13, wherein the mole ratio of the organomagnesium precursor to the titanium tetrachloride or titanium haloalkoxo species is 1:13.

5 16. Single step process as claimed in claim 13, wherein the titanium tetrahalide is titanium tetrachloride.

17. Single step process as claimed in claim 13, wherein the mole ratio of aluminium in the cocatalyst to titanium in the procatalyst is 200 : 1.

10

18. Single step process as claimed in claim 13, wherein the solvent is chlorobenzene.

15

19. Single step process as claimed in claim 13, wherein the microwave radiation of 300 W is applied.

20. Single step process as claimed in claim 13, wherein the organoaluminium compound is triethyl aluminium.

20

21. Single step process as claimed in claim 13, wherein the selectivity control agent is p-ethoxy ethyl benzoate or dicyclohexyl dimethoxy silane or diphenyl dimethoxy silane.

5 22. Single step process as claimed in claimed 13, wherein the mole ratio of the selectivity control agent to titanium is 10 - 75 : 1.

23. Single step process as claimed in claim 13, wherein the molar ratios of electron donor and acid halide, if any to titanium are 0.7 and 0.07, respectively.

24. Single step process as claimed in claim 13, wherein the electron donor is ethyl benzoate, dibutyl or diisobutyl phthalate.

15 25. Single step process as claimed in claim 13, wherein the acid halide is benzoyl chloride.

26. Lower α -alkene polymerisation heterogeneous solid catalyst obtained by the single step process as claimed in anyone of claims 13 to 25.

27. A process for polymerisation of lower α -alkene with a heterogeneous solid catalyst as claimed in claim 12 or 26 under polymerisation conditions in known manner.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN 03/00152-0

CLASSIFICATION OF SUBJECT MATTER

IPC⁷: C08F 10/00, C08F 2/46, C08F 4/654

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁷: B01J, C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|--|-------------------------------|
| A | GB 1530445 A (THE BRITISH PETROLEUM COMPANY) 1 November 1978 (01.11.78) <i>claims 1,4,8.</i> | 1,4,5,9,12,13, 15-17,26,27 |
| | ---- | |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/IN 03/00152-0

| Patent document cited in search report | | | Publication date | Patent family member(s) | Publication date |
|---|---|---------|---------------------|----------------------------|---------------------|
| GB | A | 1530445 | 01-11-1978 | none | |
| GB | A | 1530445 | 01-11-1978 | | |